Standard Operating Procedure for Total Nitrogen in Sediments by Alkaline Persulfate Oxidation Digestion (Lachat Method)

LG602

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1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the various species of nitrogen compounds, excluding nitrogen gas in sediment matrices oxidized to nitrate by alkaline potassium persulfate digestion.

1.2 The approximate working range is 0.03 to 20.00 mg N/L.

2.0 SUMMARY OF METHOD

2.1 Nitrogen compounds are oxidized to nitrogen in alkaline persulfate spontaneously when the media is autoclaved under 15 psi and 121°C. Nitrogen losses are not observed when oxidation occurs under these pressure conditions.

2.2 Nitrate is quantitatively reduced to nitrite by passage of the sample through a column containing copper coated cadmium. The nitrite (reduced nitrate plus original nitrite) is determined by diazotizing with sulfanilamide dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Sediment samples are stored in a 500-mL plastic bottles at approximately 4°C.

4.0 INTERFERENCES

4.1 Residual chlorine can interfere by oxidizing the cadmium column.

4.2 A major interference can come from ammonia contamination of glassware or reagents. To prevent this, glassware and utensils should be washed in 1N hydrochloric acid and stored in an ammonia-free environment. Use only high purity potassium persulfate and store in a dry ammonia-free environment.

4.3 The total carbon content of the sample in excess of 20 mg C/L may interfere with the completion of the alkaline persulfate oxidation.

5.0 APPARATUS AND SUPPLIES

5.1 50-g capacity porcelain drying dishes

5.2 Mortar and pestle

5.3 Desiccator

5.4 60-mL glass digestion tubes with plastic Teflon-lined caps

5.5 Drying oven

5.6 Autoclave

5.7 Automatic pipet, calibrated to 10.0 mL.

5.8 Plastic disposable pipet tips

5.9 Lachat QuikChem AE

5.9.1 XYZ sampler

5.9.2 Nitrate/nitrite manifold (Lachat Method # 31-107-04-1-B)

5.9.3 Cadmium-copper reduction column

5.9.4 Printer

NOTE: *Replacement cadmium columns are obtained from Lachat Instruments.*

6.0 REAGENTS AND STANDARDS

6.1 All reagents should be stored in the appropriate bottles and labeled with the following information:

Identity	(15 N Sodium hydroxide)
Concentration	(1000 mg N/L)
Date of Preparation	(mm/dd/yy)
Expiration Date	(mm/dd/yy)
Initials of Preparer	(IMF)

6.2 **Use reagent water for all solutions.**

6.3 **15 N Sodium Hydroxide:** Add 150 g of NaOH to 250 mL of water.

CAUTION: *The solution will get very hot!* Swirl until dissolved. Cool and store in a plastic bottle.

6.4 **Ammonium Chloride Buffer, pH 8.5:** In a fume hood, to a 1-L volumetric flask, add approximately 250 mL reagent water and 105 mL HCL. Slowly add 95 mL of ammonium hydroxide (NH_4OH). Stir very carefully. This liquid fumes and may spew. Add 1.0 g disodium ethylenediamine tetra acetic acid dihydrate ($Na_2EDTA•2H_20$). Adjust pH to 8.5 with 15 N NaOH and dilute to 1 L. Degas with Helium prior to use.

6.5 **Sulfanilamide Color Reagent:** To a 1-L volumetric flask add about 600 mL water. Then add 100 mL of 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N-(1-naphthyl) ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve. Dilute to the mark,

and invert to mix. Store in a dark bottle. This solution is stable for one month. De-gas with Helium prior to use.

6.6 **3.75 N Sodium Hydroxide:** Add 37.5 g of NaOH very slowly to 250 mL of water.

6.7 Preparation of Calibration Standards

6.7.1 **Stock 1000 mg N/L Nitrate Solution:** Dissolve 7.218 g of potassium nitrate (KNO_3), dried for 1 hour at 105°C, in 500 mL of DI water and dilute to 1 L.

6.7.2 **Working Standards:** Prepare standards over the range of analysis. For the working range of 0 - 20.00 mg N/L, the following standards may be used:

mL of Stock Standard Solution (6.7.1) diluted to 1 L	Concentration mg N/L
0.0	0.00
0.2	0.20
0.4	0.40
1.0	1.00
4.0	4.00
8.0	8.00
20.0	20.00

6.8 Preparation of Control Standards

6.8.1 **Stock 1000 mg N/L Nitrate Control Standards:** Any nitrate compound may be used for control standards. The control standards should be prepared by someone other than the analyst. Weigh 2.6795 g of glycine ($NH_2CH_2CO_2H$), dried at 75°C for 1 hour, and dissolve in 250 mL of DI water. Dilute to 0.5 L in volumetric flask with DI water. The **Organic Spike** is prepared by adding 1.00 mL of the 6.8.1 standard to 40 mL of sample.

6.8.2 Prepare the control standards using solution (6.8.1).

QC Type	mL of Control Standard Solution (6.8.1) diluted to 1 Liter	Concentration mg/L
Low Check Standard (CL)	5.0	5.00
High Check Standard (CH)	16.0	16.00

7.0 PROCEDURE

7.1 Soak the 50-g capacity porcelain drying dishes, mortars, pestles, digestion tubes, Teflon-lined caps and utensils in 10% sulfuric acid for one hour. Rinse three times in reagent water and dry at 105°C. Place the porcelain drying dishes in a desiccator to cool.

7.2 Record the mass in grams of the empty porcelain drying dish on the Sample Preparation Log Sheet in the column labeled "Weight of Dish."

7.3 Fill each porcelain drying dish to capacity. Record the mass in grams of the filled porcelain drying dishes on the Sample Preparation Log Sheet in the column labeled "Weight of Dish and Wet Sample." Place samples in the oven at 105-110°C overnight or for no less than eight hours. Cool samples in the desiccator to room temperature. Weigh and record dried sample on the Sample Preparation Log Sheet in the column labeled "Weight of dish and dry sample".

7.4 Place one sample in the oven again at 105-110°C for an additional hour to check for constant weight. After the sample have cooled to room temperature in the desiccator weigh and record as described previously. Compare the mass between the overnight weight and the weight after the additional hour.

NOTE: *In the event that the mass difference between the overnight drying weight and the drying weight plus one hour is greater than 0.5000 grams, repeat step 7.4.*

7.5 Calculate % moisture.

7.6 Digestion Procedure

7.6.1 Weigh approximately 0.2-0.4 g of uniform wet sample. Record the weight of the sample on the Sample Preparation Log Sheet in the column labeled "Weight of Sample in Digestion Tube".

7.6.2 Transfer sample to a 60-mL test tube. Add 40 mL of DI water, 1.0 g of potassium persulfate ($K_2S_2O_8$) and 1 mL of 3.75M NaOH. Close with cap.

7.6.3 To cleaned, dried tubes, add 40 mL of working calibration standards, control standards, and blanks. Add 1.0 g of potassium persulfate ($K_2S_2O_8$) and 1 mL of 3.75M NaOH. Close with cap.

7.6.4 Autoclave samples and standards for 45 minutes at 15 psi and 121°C. Bring the samples to the room temperature and add 1 mL of 3.75M NaOH.

7.7 Follow the Lachat Procedural SOP.

8.0 CALCULATION

8.1 The computer yields results in mg N (as NO_2+NO_3)/L.

8.2 Calculation of total nitrogen in sediments

$$\textit{Total Nitrogen (mg/g dry weight)} = \frac{\textit{Concentration of nitrogen from instrument (in mg N/L)} \times 4}{\textit{Weight of wet sediment sample in grams} \times (100 - \textit{\% moisture})}$$

9.0 QUALITY CONTROL

9.1 The following items are required with the minimum frequency indicated.

Audit	Type	Frequency	Limits
High Check (CH)	Method	Beginning, End, 1/40 Sample	16.00 ± 1.60
Low Check (CL)	Method	Beginning, End, 1/40 Sample	5.00 ± 0.50
Reagent Blank (RB)	Method	Beginning, End, 1/40 Sample	0.00 ± 0.08
Duplicate	Method	1/40 Sample	RPD ≤20%
Spike (organic)	Method	1/40 Sample	100% ± 20%

10.0 WASTE DISPOSAL

10.1 Effluent from this analysis should be neutralized with sodium hydroxide to a pH of 6-9 and then washed down the laboratory drain with plenty of water.

11.0 PREVENTATIVE MAINTENANCE

11.1 Required maintenance is described in the Lachat Procedural SOP.

12.0 TROUBLESHOOTING

12.1 The most common problem is deactivation of the cadmium column which results in low values and non-linear calibration curves. The deactivation of the column is quantified by a column having less than a 90% efficiency factor. To determine cadmium column efficiency, prepare a 0.600 mg N as NO_2/L solution.

12.2 Preparation of the Sodium Nitrite Column Efficiency Test Standards

12.2.1 To prepare the 100 mg N (as NO_2) nitrite stock standard, dissolve 0.4926g sodium nitrite ($NaNO_2$), dried for 1 hour at 105°C, in 500 mL of DI water. Add 1 mL of H_2SO_4 (conc.) and dilute to 1 L. Mix this solution thoroughly.

12.2.2 From the 12.2.1 stock solution take 6.0 mL and add this to 500 mL DI water and dilute to 1 L. The concentration of this solution is 0.60 mg N (as NO_2)/L. Store in a plastic container at 4°C.

12.2.3 From the 6.9.2 stock solution, take 6.0 mL and add this to 500 mL DI water and dilute to 1 L. The concentration of this solution is 0.60 N (as NO_3)/L. Store in a plastic container at 4°C.

12.3 The cadmium column efficiency is calculated by comparing the known concentration of the 0.60 mg N (as NO_3)/L (12.2.3) to the known concentration of 0.60 mg N (as NO_2)/L (12.2.2). The acceptable efficiency is ≥ 90%.

$$Percent\ Efficiency = \frac{Concentration\ NO_3}{Concentration\ NO_2} \times 100\%$$

12.4 The efficiency test should be performed monthly.

13.0 REFERENCES

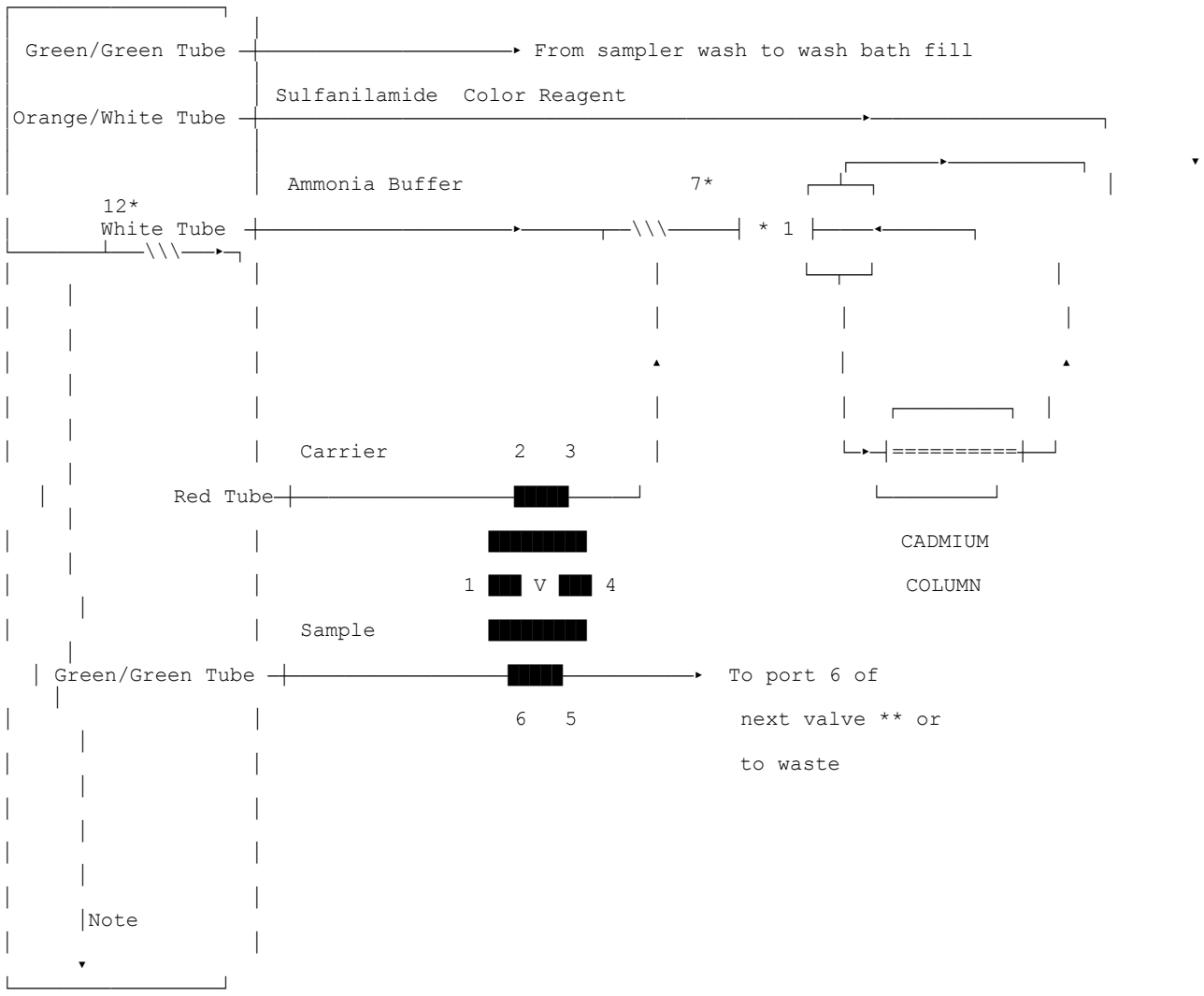
13.1 Lachat Instruments, QuikChem Method 10-107-04-1-A. Nitrate/Nitrite in Surface and Wastewaters by Flow Injection analysis. Revision Date: 6 January 1999.

13.2 Lachat QuikChem AE Operating Manual.

Sample Preparation Log Sheet

Sample and Dish ID	Weight of Dish (g) (A)	Weight of Dish and Wet Sample (g) (B)	Weight of Dish and Dry Sample (g) (C)	Weight of Dish and Sample After Drying an Additional Hour (g)	Weight of Wet Sample (g) (B-A)	Weight of Dry Sample (g) (C-A)	% of Moisture $\frac{(B-C)*100\%}{(B-A)}$	Weight of Sample in Digestion Tube (g)

NITRATE-NITRITE ANALYTICAL MANIFOLD



Legend

7
\\\ :is 135cm of tubing on the 7cm coil support

12
\\\ :is 255cm of tubing on the 7cm coil support

2 3
1 V 4 : 6 Port Valve
5 6

Comments

* 1. This is a 2-state switching valve used to place the cadmium column in-line with the manifold.

State One: Nitrate + Nitrite	State Two: Nitrite
Solution flow is through the cadmium column.	Solution flow by-passes the cadmium column.

2. Filter used is 520 nm.
3. Sample loop - QC8000 Microloop
4. All manifold tubing is 0.5 mm (0.022") ID. This relates to a flow of 2.5 µL/cm.
5. The Carrier is helium degassed DI Water.
** This will occur if more than one parameter is being run simultaneously.

Note: Backpressure loop of 100 cm x 0.0022" i.d. tubing